

Anticorrosion Coatings

Can They Be Made without Chromium?

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Chromium is a surprisingly common ingredient in anticorrosion coatings such as the paint pretreatment being sprayed on the airplane fuselage below. Even the stainless steel cutlery that most of us use daily has a native coating of chromium oxide. But the Strategic Environmental Research and Development Program is looking for an alternative because chromium ions are a serious health threat when inhaled or ingested by metal workers during metal coating and stripping. Recent neutron reflectometry studies at the Los Alamos Neutron Science Center explore whether thin films of silane could afford equivalent corrosion protection.

Technicians must wear complete protective clothing as they apply chromate conversion coating to a commercial aircraft. The chromate must be recovered from the overspray.



The 2000 David and Goliath film *Erin Brockovich* pits the heroine, Brockovich, against corporate giant Pacific Gas and Electric (PG&E). The film is based on one of the most lucrative legal cases in history (\$333 million). The suit revolves around hexavalent chromium (Cr^{6+}) used by PG&E to control corrosion in cooling towers in its Hinkley, CA, compressor station. PG&E would periodically treat the surface of the cooling coils and release the chromium-containing wastewater into ponds leading to contamination of the Hinkley air and groundwater. Like most heavy metals, Cr^{6+} is toxic and a suspected carcinogen, the release of which is regulated by the Environmental Protection Agency and the Occupational Safety and Health Administration, as well as state agencies.

In spite of its toxicity, Cr^{6+} remains an essential ingredient in the metal finishing industry for corrosion control. No substitutes perform as well as Cr^{6+} , particularly at high temperature. Cr^{6+} is used as a metal pretreatment and is also found in slightly soluble pigments in paint primers (Figure 1). When Cr^{6+}

comes in contact with most metals, it forms a passive oxide layer called a chromate conversion coating (CCC), which is resistant to most types of corrosive attack. If the oxide layer is scratched, chromium leaches from the pigment and heals the damage.

Chromium oxide itself is not harmful. Health concerns arise primarily during coating application and removal. In fact, chromium oxide exists as protective film on stainless steels, which most of us put in our mouths every day in the form of stainless steel tableware. During application of paint pretreatment, however, soluble salts of chromium are used, which are hazardous. Workers must be protected and recovery costs of the overspray are high (see photo on opposite page). Airborne hazards also exist when the coating is stripped.

Silane Anticorrosion Coatings

Because of the above considerations, the Strategic Environmental Research and Development Program (SERDP) (www.SERDP.org) funds an

extensive research effort to develop alternatives to chromate coating systems used in the Department of Defense. The goal is to completely eliminate Cr^{6+} without introducing other hazardous substances or air pollutants. The SERDP at the University of Cincinnati, for example, exploits inorganic silane polymers deposited from solutions of water-soluble precursors. Bis-type silanes (Figure 2) are particularly effective. These silanes are water soluble and polymerize to corrosion-resistant coatings.

Two alternative coating systems are under development at Cincinnati (Figure 1). In the “silane” system, highly crosslinked silane polymers replace the chromate conversion coating. In the “superprimer” system, silanes are incorporated into water-soluble epoxy and urethane polymer precursors. These precursors cure through crosslinking to a protective film that replaces both the chromate conversion coating, as well as the pigment-containing primer. Figure 3 compares the corrosion performance of conventional chromate-pretreated aluminum alloy with that of the same

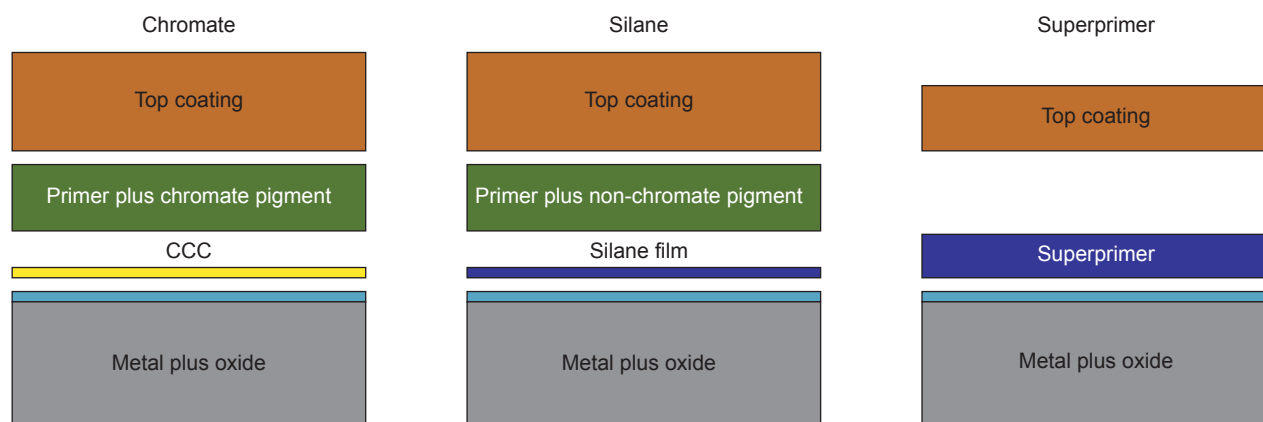


Figure 1. Schematic of Chromate and Silane-Based Coating Systems

(a) In the chromate system, chromium salts are used in the chromate conversion coating (CCC) and in the pigments in the primer. These pigments slowly leach chromium, which heals any damage to the CCC. (b) In the silane system, the CCC is replaced by a silane film and nonchromate corrosion inhibitors are used in the primer. (c) In the superprimer concept, the silane and primer are combined in a one-step superprimer.

material coated with a silane film.

As part of the SERDP, the Cincinnati team collaborates with scientists at Los Alamos and Sandia National Laboratories to elucidate the properties, protection mechanism, and vulnerabilities of silane-based protective coatings. This research exploits the Surface Profile Analysis Reflectometer (SPEAR) at the Manuel Lujan Jr. Neutron Scattering Center (see the article “The Hydrophobic Effect—Why Do Raindrops Slide off Leaves?” on page 164 for a description of SPEAR). One of the issues we investigated is the so-called mixed-silane effect. As part of this effort, we discovered some unexpected properties of hydrophobic silanes, namely, that they are not particularly hydrophobic.

The Mixed-Silane Effect

The mixed-silane effect is observed in mixtures of the two bis-silanes shown in Figure 2. These silanes exhibit contrasting behavior, traceable to the bridging group (the amine group NH vs the sulphur group S_4). Corrosion tests show that bis-amino silane does not offer good corrosion protection on either aluminum alloys or galvanized steel. The more hydrophobic bis-sulfur silane, on the other hand, is slow to react, has poor wetting properties, and is not effective on galvanized steel. Interestingly, a bis-sulfur/bis-amino (3/1) mixture shows enhanced performance compared with the two individual silanes and provides protection for many metals including aluminum alloys and galvanized steel.

To study the films using neutron reflectivity, the silanes are spin-coated on silicon substrates from prereacted silane solutions. Spin-coating is a procedure to produce a very uniform film. A solution containing the silanes is spread in excess on a silicon wafer of the type used in the electronics indus-

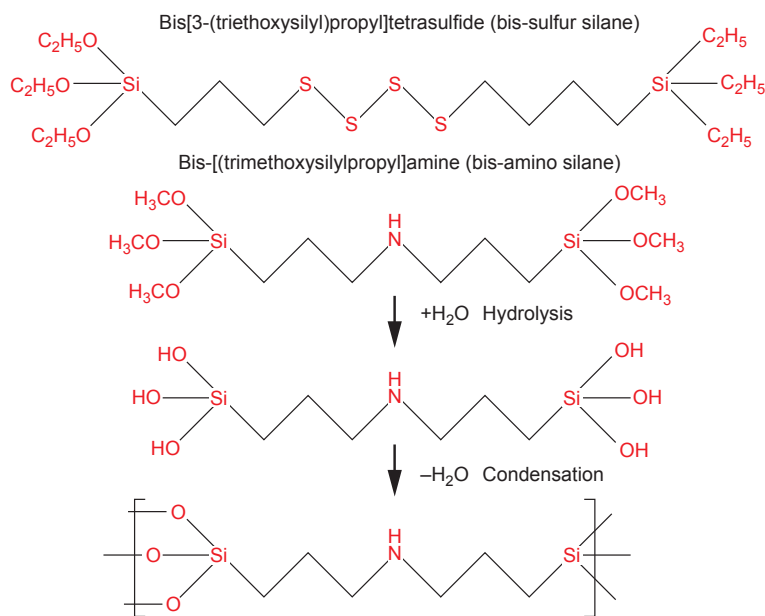


Figure 2. Two Bis-Silanes for Silane-Based Protective Films

Bis-silanes have six alkoxy groups that undergo hydrolysis and condensation to form silicon-oxygen-silicon (Si-O-Si) bonds, leading to a highly crosslinked film. These reactions are shown for the bis-amino compound. In their polymerized state, bis-sulfur is hydrophobic and bis-amino is hydrophilic. Water-soluble mixtures of these two silanes lead to effective protective films.

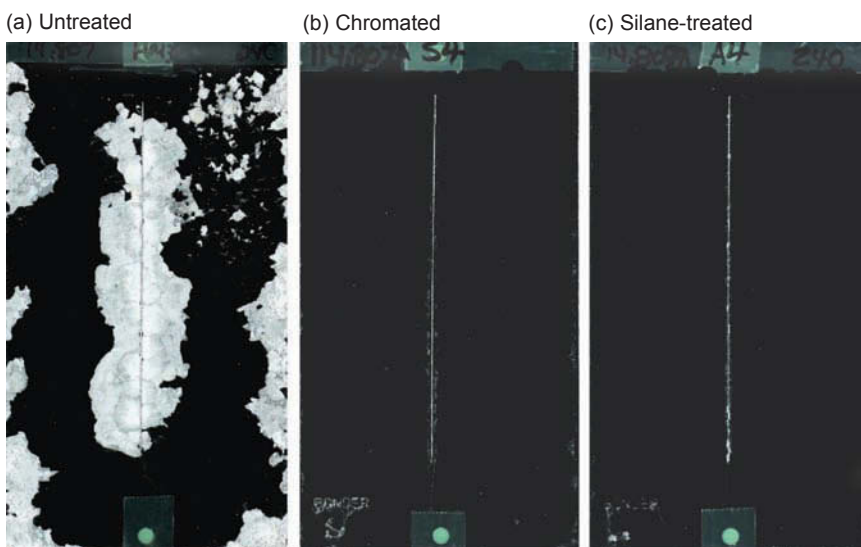


Figure 3. Responses of Aluminum Surfaces to Corrosive Salt Spray Aluminum alloy (5005) coupons with different surface coatings were exposed to 240 h of copper-accelerated acetic-acid salt spraying. All three panels had a polyurethane powder-paint overcoat. The silane panel was pretreated with a 3/1 mixture of the bis-sulfur and bis-amino silane. The chromated panel (b) shows less scratch corrosion than the silane-treated panel (c). The self-healing character of the chromate conversion coating is responsible for this effect.

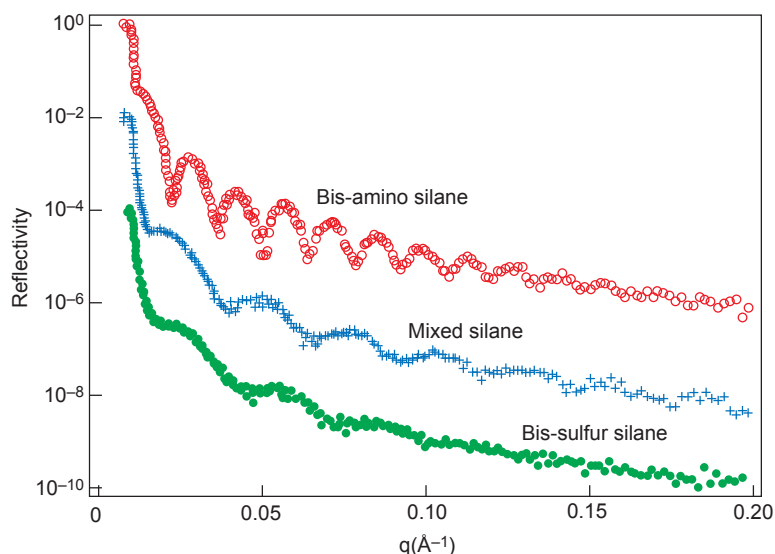


Figure 4. Reflectivity Curves for As-prepared Bis-Amino, Bis-Sulfur, and Mixed Silane

For clarification, the reflectivity curve of mixed silane is suppressed by 10^2 , and the reflectivity curve of bis-sulfur silane is suppressed by 10^4 . The thickness of the films can be calculated from the distance between the fringes, Δq , as $2\pi/\Delta q$. The fringes are the most distinct in the bis-amino film, indicating this film is the smoothest. Bis-sulfur is the thinnest and roughest. The mixed film shows intermediate behavior.

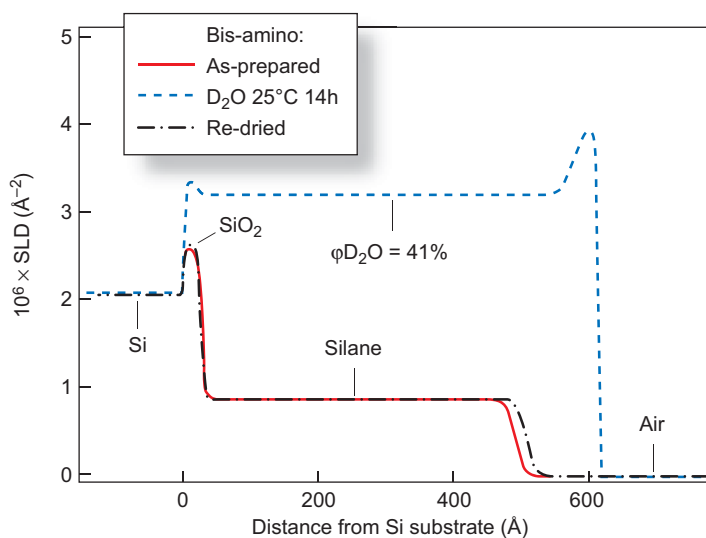


Figure 5. Scattering-Length-Density (SLD) Profiles for Dry, Water-Conditioned, and Redried Bis-Amino Films Coated on Silicon

These profiles were obtained assuming a layered model and then inverting neutron reflectivity data. From the SLD of the dry film (solid red curve), we know the film is fully condensed, or crosslinked. After exposure to D_2O vapor for 14 h, the blue curve is obtained. The SLD of the swollen film is now much higher due to absorption of D_2O , whose SLD is six times larger than that of the dry film. The volume fraction ϕ of D_2O in the film is calculated from the SLD to be 41%. That is, 41% of the volume is occupied by D_2O even though the film swells by only 25%. This high water content is due to the hydrophilic nature of the NH group in the bridge (Figure 2). The film returns almost to the pristine state on redrying, showing that there is no chemical alteration due to water exposure at room temperature.

try. Then the wafer is spun up to 2000 revolutions per minute to strip off the excess solution, leaving a silane film a few hundred angstroms thick. One angstrom is 10^{-10} meter.

Figure 4 compares the neutron reflectivity curves for bis-sulfur, bis-amino, and a 3/1 mixture of the two. The data are plotted as reflectivity (fraction of the neutron beam reflected) vs momentum transfer, q . Momentum transfer is chosen as the independent variable rather than the reflection angle because there is no unique reflection angle at a pulsed neutron source where neutrons with a range of wavelengths impinge on the sample. Also, in the Fourier transform that approximately relates reciprocal-space data (Figure 4) to real-space mass distribution (as in Figure 5), q is the variable conjugate to the spatial coordinate, z , where z is the distance normal to the silicon wafer surface and therefore through the thickness of the film.

Simple observation of the curves in Figure 4 reveals that there is nothing special about the mixed silane. For example, the spacing of the mixed-film fringes, which reveals the film thickness, lies between that of the two neat films. What is really of interest, however, is the response of the films to water. To examine this issue, the films in Figure 4 were exposed to water vapor, and neutron reflectivity was used to examine water penetration. The films were studied dry, in the presence of water vapor and in the redried state. Comparison of the data for the as-prepared and redried films reveals whether the films are chemically modified by exposure to water vapor.

Dry-Film Properties

If the dry as-prepared bis-amino reflectivity data in Figure 4 are inverted, the neutron scattering-length-density (SLD) profile in Figure 5 (red line) is obtained. The

SLD is the neutron scattering power of a material. In Figure 5, for example, the thin oxide layer has a higher SLD than either the substrate or the silane film. Because neutron scattering involves nuclear forces, there is no simple relationship between the SLD and the mass density. Nevertheless, the SLD is calculable for any substance of known composition and density. From the measured SLD of the dry film in Figure 5, for example, we know that the film is fully crosslinked, since all partially crosslinked candidates have a lower calculated SLD. That is, all the alkoxy groups ($\text{CH}_3\text{O-Si}$) in the dry film have hydrolyzed and condensed to form silicon-oxygen-silicon (Si-O-Si) bonds.

Water Barrier Properties

In spite of the fact that the bis-amino film is fully condensed, it swells dramatically in the presence of water vapor (blue line in Figure 5). Heavy water (D_2O , deuterium oxide) is used for this experiment because its SLD is six times greater than that of the dry film, so it is very visible to neutrons. From the SLD of the “wet” film, we calculate that D_2O occupies 41 percent of the volume. This high water content is due to the hydrophilic nature of the NH bridging group. It is interesting that the film thickness increases by only 25 percent, so some of the D_2O must invade free volume present in the dry film. If the film is redried, the SLD profile returns to the dry state (black curve), indicating that no D_2O is retained in the film and no chemical reactions occur to chemically incorporate deuterium in the film.

Another interesting aspect of bis-amino films is the hydrophilic layer at the silane–air interface. This layer is revealed in Figure 5 by the peak in the SLD at the air interface of the wet film. This peak is only observed in films containing bis-amino. This feature could be due to restructuring

of the film surface in the presence of water vapor.

Bis-sulfur films are more hydrophobic, as can be seen in Figure 6. In this case, the water-conditioned film absorbs 7.8 volume percent water, still a surprisingly large number for a hydrophobic coating. We have also studied thicker films and find that water always penetrates the film. Apparently, the protective character of silane films does not depend on strict water-barrier properties.

From the SLD of the dry bis-sulfur film, we calculate that it is less crosslinked than the bis-amino film, even though the latter absorbs four times as much water. At least 11 percent of the bis-sulfur alkoxy groups do not condense at room temperature. Having found that the bis-sulfur is more water-resistant and less crosslinked than bis-amino, we conclude that the nature of the bridging group is more important than the crosslink density in controlling the water barrier properties.

Mixed Films

So what is it about the mixed film that exhibits superior properties in corrosion tests? It turns out that all the properties of the mixed film lie between those of the bis-amino and bis-sulfur films (Figure 7). The SLD, water uptake, film thickness, and film roughness are just the weighted average of the neat-film values. The water content of the wet mixed film, for example is 12.6 percent compared with 7.8 percent for bis-sulfur and 41 percent for bis-amino. The mixed film, however, does show the same hydrophilic layer at the air interface found in the neat bis-amino film. This layer provides a clue regarding the improved performance of the mixed film.

The mixed silane effect is probably related to the buffering and catalytic effect of the amine group on the bis-

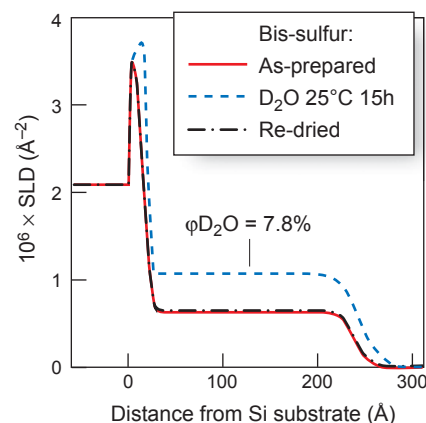


Figure 6. SLD Profile for Bis-Sulfur Bis-sulfur is hydrophobic, leading to less water absorption than bis-amino. Nevertheless, water penetrates all the way to the oxide surface on the silicon wafer. No deuterium-rich layer is observed at the air-side surface although there is some modification at the wafer–film interface.

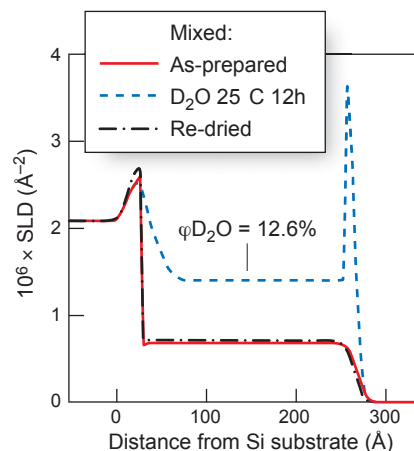


Figure 7. SLD Profile for Mixed Silane The 12.6% water content in the mixed-silane film lies between that of bis-amino and bis-sulfur. The peak in the SLD at the air interface is seen only for films containing bis-amino. The amino groups must alter the near-surface region in such a way as to attract water. The modified surface also improves bonding to primer overcoats.

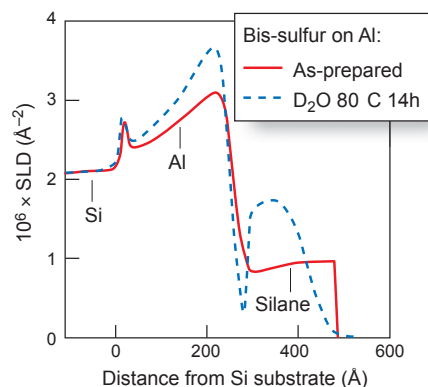


Figure 8. SLD Profile for Bis-Sulfur on Aluminum
Aluminum is sputter-deposited on a silicon wafer, and then the surface is spin-coated with silane. The highly distorted profiles are attributed to an etching effect of the acidic bis-sulfur on the aluminum and its native oxide. The increased SLD in the aluminum region is attributed to absorption of D_2O in a porous aluminum oxide layer.

amino moiety. That is, the amine group catalyzes the condensation of bis-sulfur, leading to more crosslinked films as the film ages. This polar (hydrophilic) group also improves the wettability of the mixed silane and moderates the acidic nature of the bis-sulfur. The wettability issue is relevant at both the metal-silane and the silane-air interfaces. Regarding the metal interface, wetting films form more-uniform coatings. At the air interface, the presence of the amino-induced hydrophilic layer enhances bonding to primers and paints.

The buffering effect of bis-amino on bis-sulfur can be appreciated by considering the SLD profile of bis-sulfur on aluminum rather than silicon. To study film on aluminum, we first sputter-deposit aluminum on the silicon wafer and then spin-coat the silane film. The reflectivity data are difficult to fit, and the resulting SLD profile is highly distorted (Figure 8). Because the natural pH of bis-sulfur solutions is acidic, the aluminum sur-

face is etched by the coating solution. In the mixed silane, however, bis-sulfur is buffered by the amino group of bis-amino, and excellent films are obtained on aluminum. The mixed-silane effect, therefore, is not due to any special barrier properties of the film, but to the interaction of the film with both the substrate and overcoat.

Processing Conditions

We are investigating a number of other issues regarding silane-based protective coatings. Given that silanes are not rigorous water barriers, we want to know if polymer-silane superprimers have better water-barrier properties. We are also investigating issues related to curing and aging of the films. Finally, given that water penetrates all water-borne silanes, it is likely that the corrosion inhibition is related to control of transport of ionic species such as chloride. Monitoring chloride by neutron reflectivity is very challenging, however, because it is present at low concentration. Nevertheless, we can explore how films degrade in the presence of such aggressive ions.

Conclusions

The elimination of Cr^{6+} in the metal finishing industry is a multibillion-dollar challenge. Our research shows that the protection of metals is a complex problem that is not fully understood. Regardless of which alternative to Cr^{6+} is selected, a thorough understanding of the properties and vulnerabilities of the alternative will be required. Neutron reflectivity will continue to provide critical data on the morphology and water response of candidate metal-protection systems. ■

Further Reading

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